

REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-02-

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1. REPORT DATE (DD-MM-YYYY) 10/24/02		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 03/01/99 to 08/31/02	
4. TITLE AND SUBTITLE Photon-Gated Photorefractive Polymers				5a. CONTRACT NUMBER F 49620-99-01-0021	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER 61102F	
6. AUTHOR(S) Nasser Peyghambarian Bernard Kippelen				5d. PROJECT NUMBER 2303	
				5e. TASK NUMBER 2303/CX	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Arizona Board of Regents, University of Arizona PO Box 3308 Tucson, AZ 85722-3308				8. PERFORMING ORGANIZATION REPORT NUMBER FRS #311800	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Office of Scientific Research 801 N. Randolph St., Ste. 732 Arlington, VA 22203.1977				10. SPONSOR/MONITOR'S ACRONYM(S) AFOSR	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approve for Public Release; Distribution Unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT The goal of this program on Photorefractive polymers are to improve the performance of Photorefractive polymers and to fabricate innovative devices based on these highly efficient materials. During the lifespan of the program we have made significant progress in the following areas: (i) material fabrication and characterization, (ii) modeling of photorefractivity in polymers and (iii) development of new applications based on photorefractive polymers. During the course of the investigation we published (with AFOSR acknowledgments) 12 papers in refereed journals and 5 book chapters and gave 32 invited talks at international conferences and workshops.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES 8 + 1 Cover	19a. NAME OF RESPONSIBLE PERSON Nasser Peyghambarian
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (include area code) (520) 621-4649

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Final report

Under current AFOSR grant # F49620-99-1-0021 for which I was a co-Investigator with Prof. Nasser Peyghambarian who was the principal investigator, we have obtained numerous significant results in the development of photorefractive polymers for holographic storage and optical processing applications. During the course of this investigation we published (with AFOSR acknowledgments) 12 papers in refereed journals and 5 book chapters and gave 32 invited talks at international conferences and workshops.

The goals of our AFOSR program on photorefractive polymers were to improve the performance of photorefractive polymers and to fabricate innovative devices based on these highly efficient materials. A central objective of our program was to achieve destructive read-out in an organic photorefractive material. This was achieved recently and the work will appear in December 2001 in *Optics Letters*. It can be considered a major milestone in the development of photorefractive polymers.

During the lifespan of the program we have made significant progress in the following areas: (i) material fabrication and characterization; (ii) modeling of photorefractivity in polymers; (iii) development of new applications based on photorefractive polymers. Specifically:

- We demonstrated the recording of holograms and their non-destructive read-out in a photorefractive polymer using two-photon absorption. Sensitivity was provided by the excitation of the electro-active chromophore with femtosecond pulses followed by charge injection into the photoconducting PVK matrix. The holograms could be fully erased with a pulsed laser source but were insensitive to cw laser beams with the same wavelength. Studies of the field and intensity dependence of the diffraction efficiency indicate that the holograms are formed through the photorefractive effect. In our experiments we used 105 μm -thick samples of the photorefractive polymer composite FTCN:PVK:BBP:ECZ (25:55:10:10 wt. %) sandwiched between two ITO coated transparent electrodes. The composite contained the electro-active chromophore FTCN, the photoconducting polymer matrix poly(*N*-vinylcarbazole) (PVK), and the plasticizers *N*-ethylcarbazole (ECZ) and benzyl butyl phthalate (BBP). Sensitization in this case was achieved through TPA in the electro-active dopant molecule FTCN. As shown in Fig. 1, these new samples are yellow and have no linear absorption at the operating wavelength of 650 nm. Holographic recording was achieved through four-wave mixing experiments with 130 fs pulses at a wavelength of 650 nm produced at a repetition rate of 1 kHz by an optical parametric amplifier pumped by the amplified output of a Ti:Sapphire laser system. To demonstrate non-destructive read-out we changed the wavelength of the pulsed laser source experiments to 700 nm and replaced the pulsed reading beam with a cw laser diode emitting at the same wavelength. No changes in diffraction efficiency could be detected for several minutes with a reading power as high as 5 mW, that is an order of magnitude higher than the average power of the pulsed writing beams. However, when one of the pulsed writing beams was blocked, the grating could be erased completely within a few seconds by the remaining spatially uniform writing beam.

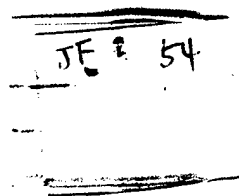


Fig. 1: Photograph of a photorefractive polymer sensitized by two-photon absorption.

- We demonstrated the fabrication of photorefractive polymer composites using injection molding (see Fig. 2). This work is a proof-of-principle demonstration that photorefractive polymers can be fabricated using mass production techniques. For our experiments we formulated a photorefractive composite that was known to have good phase stability properties and a high dynamic range. The inert polymer was a commercial birefringence-free acrylic resin, doped with the photorefractive chromophore 2, N, N-dihexylamino-7-dicyano-methyl-idenyl-3, 4, 5, 6, 10-pentahydro-naphthalene (DHADC-MPN), that provides simultaneously transport properties and electro-activity. The composite was plasticized using diphenyl isophthalate (DIP), and sensitized using (2,4,7-trinitro-9-fluorenylidene)-malononitrile (TNFDM).

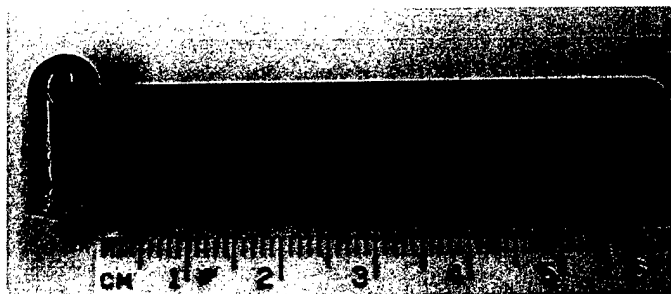


Fig. 2: Photograph of a photorefractive polymer sample fabricated by injection molding

- By getting more insight into the formation of photorefractive traps and by controlling its concentration by adjusting the relative energies of the HOMO levels of the different constituents in photorefractive polymer composites we have been able to fabricate new materials that combine high dynamic range and fast response time. By using two different plasticizers, we obtained new composites in which overmodulation of the diffraction efficiency is observed at 60 V/ μm with response times that are video compatible.
- A photorefractive polymer composite with a 2-millisecond response time was developed. To the best of our knowledge, this is the fastest response time yet reported in a polymer. Transient ellipsometric measurements directly confirm that in this system

chromophore orientational time does not limit the photorefractive response-time (Fig. 3). These new, fast materials are based on a fluorinated chromophore which combines good stability and high orientational mobility with useful dynamic range.

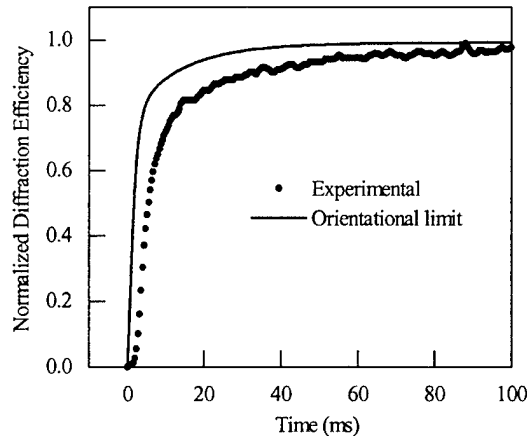


Fig. 3: Build-up dynamics of a hologram recorded in the photorefractive polymer composite FTCN:PVK:ECZ:TNFDM with a 2 ms time constant. The solid curve is the calculated build-up dynamics assuming that the orientational dynamics of the chromophore is the limiting factor.

Publications:

- 1) "Photorefractive polymer composites fabricated by injection molding," J. A. Herlocker, C. Fuentes-Hernandez, J. F. Wang, Q. Zhang, S. R. Marder, N. Peyghambarian, and B. Kippelen, submitted to Appl. Phys. Lett. (2001).
- 2) "Photorefractive properties of polymer composites fabricated by injection molding," J.A. Herlocker, C. Fuentes-Hernandez, J.F. Wang, N. Peyghambarian, Y. Zhang,⁽¹⁾ S. R. Marder,⁽¹⁾ B. Kippelen, CLEO Technical Digest p. 399 (2001).
- 3) "Photorefractive polymers sensitized by two-photon absorption," P. A. Blanche, B. Kippelen, A. Schülzgen, C. Fuentes-Hernandez, G. Ramos-Ortiz, J. F. Wang, E. Hendrickx, S. R. Marder, N. Peyghambarian, to appear in Opt. Lett. (2001).
- 4) "Optimization of photorefractive polymers doped with styrene-based chromophores," C. Fuentes-Hernandez, J. A. Herlocker, J. F. Wang, N. Peyghambarian, Y. Zhang, S. R. Marder, and B. Kippelen, SPIE Vol. 4279, p. 63 (2001).
- 5) "Photorefractive polymers" B. Kippelen, to appear in Ninth edition of the McGraw Hill Encyclopedia of Science and Technology (2001).

- 6) "Stabilization of the response time in photorefractive polymers," J. A. Herlocker, C. Fuentes-Hernandez, K.B. Ferrio, E. Hendrickx, Y. Zhang, J.F. Wang, P.A. Blanche, S. R. Marder, N. Peyghambarian, B. Kippelen, *Appl. Phys. Lett.* **77**, 2292 (2000).
- 7) "On the mechanism of orientational photorefractivity in polymer dispersed nematics," A. Golemme, B. Kippelen, N. Peyghambarian, *Chem. Phys. Lett.* **319**: (5-6) 655-660 (2000).
- 8) "*Photoconductive fatigue studies in fast photorefractive polymers*," J. A. Herlocker, K.B. Ferrio, E. Hendrickx, Y. Zhang, J.F. Wang, E. Mash, N. Peyghambarian, and B. Kippelen, submitted to ACS national meeting Fall, Symposium on Organic Thin Films for photonic Applications, *Proc. Am. Chem. Soc* **83**, 190 (2000).
- 9) "High photogeneration efficiency of charge transfer complexes formed between low ionization potential arylamines and C₆₀," E. Hendrickx, B. Kippelen, S. Thayumanavan, S. R. Marder, A. Persoons, and N. Peyghambarian, *J. of Chem. Phys.* **112**, 9557-9561 (2000).
- 10) "Stabilized response-time in a photorefractive polymer composite doped with a styrene chromophore and C₆₀," K.B. Ferrio, J. A. Herlocker, E. Hendrickx, J.F. Wang, Y. Zhang, A. P. Persoons, N. Peyghambarian, and B. Kippelen, *Conference on Lasers and Electro-optics*, 2000, Technical Digest Series, p. 9, (2000).
- 11) "Improved Photogeneration Efficiency of C₆₀ Sensitized Arylamines," E. Hendrickx, B. Kippelen, S. R. Marder, A. P. Persoons, and N. Peyghambarian, *Proceedings of ICONO 5*, Davos, Switzerland, March, Nonlinear Optics (2000).
- 12) "Photorefractive polymers with video-rate performance," N. Peyghambarian, K. B. Ferrio, J. A. Herlocker, B. D. Guenther, S. Mery, B. Kippelen, *SPIE Proc.* Vol. 3749 p. 336-337, 18th Congress of the International Commission for Optics, A. J. Glass, J. D. Goodman, M. Chang, A. H. Guenther, T. Asakura Eds., (1999).
- 13) "Charge transport and chromophore orientation in a new photorefractive polymer composite with response-time in the millisecond regime," K. B. Ferrio, J. A. Herlocker, E. Hendrickx, B. D. Guenther, N. Peyghambarian, B. Kippelen, S. Mery, *Conference on Lasers and Electrooptics*, 1999 Technical Digest Series, pp. 510-511, (1999).
- 14) "Photoconductive properties of PVK-based photorefractive polymer composites doped with fluorinated styrene chromophores," E. Hendrickx, Y. D. Zhang, K. B. Ferrio, J. A. Herlocker, J. Anderson, N. R. Armstrong, E. A. Mash, A. P. Persoons, N. Peyghambarian, B. Kippelen, *Journal of Materials Chemistry* **9**, 2251-2258 (1999).

- 15) "Photorefractive polymer composites with short response times," B. Kippelen, E. Hendrickx, K. B. Ferrio, J. Herlocker, Y. Zhang, S. R. Marder, S. Mery, J. Anderson, N. R. Armstrong, and N. Peyghambarian, *Journal of Imaging Science and Technology*, 43, 405 (1999).
- 16) "Direct observation of orientation limit in a fast photorefractive polymer composite," J. A. Herlocker, K. B. Ferrio, E. Hendrickx, B. D. Guenther, S. Mery, B. Kippelen, and N. Peyghambarian, *Appl. Phys. Lett.* 74, 2253-2255 (1999).
- 17) "Ellipsometric determination of the electric-field induced birefringence of photorefractive dyes in a liquid carbazole derivative," E. Hendrickx, B. Guenther, Y. Zhang, J. F. Wang, K. Staub, Q. Zhang, S. R. Marder, B. Kippelen, N. Peyghambarian, *Chemical Physics*, 245, 407-415 (1999).
- 18) "4 ms response time in a photorefractive polymer," J. A. Herlocker, K. B. Ferrio, E. Hendrickx, B. D. Guenther, S. Mery, B. Kippelen, N. Peyghambarian, *SPIE Proc. Vol. 3623*, p. 168-174, *Organic Photonic Materials and Devices*, B. Kippelen and D. D. C. Bradley Eds., (1999).

Book Chapters:

- 1) "Photorefractive polymers and polymer dispersed liquid crystals," B. Kippelen, A. Golemme, E. Hendrickx, J. F. Wang, S. R. Marder, and N. Peyghambarian, in *Field Responsive Polymers*, Eds. I. M. Khan and J. S. Harrison, p. 204-225, (ACS Symposium Series 726, Washington 1999).
- 2) "Advanced organic materials for optoelectronic integrated devices, interconnects, and packaging," Sandalphon, E. Hendrickx, J. Herlocker, G. E. Jabbour, Y. Kawabe, B. Kippelen, M. M. Morrell, S. E. Shaheen, D. D. Steele, J. F. Wang, and N. Peyghambarian, submitted to Plenum Press.
- 3) "Overview of Photorefractive Polymers for Holographic Data Storage," B. Kippelen, in "Holographic Data Storage" H. Coufal, D. Psaltis, G. Sincerbox, Eds., *Optical Sciences Series* (Springer Verlag, Berlin 2000).
- 4) "Lightwave manipulation using photorefractive polymers," N. Peyghambarian, B. Kippelen, K. B. Ferrio, J. Herlocker, J. L. Maldonado, E. Hendrickx, S. Mery, A. Golemme, S. R. Marder, in "Light Wave Manipulation," Miyata and Sasabe Eds. (2000).
- 5) "Photorefractive Polymers and Their Applications," B. Kippelen and N. Peyghambarian, in *Advances in Polymer Science: "Polymers for Photonics Applications"*, K. Lee Editor, Springer Verlag, Berlin (2001).

Invited presentations:

- 1) "Photorefractive polymers with non-destructive read-out," B. Kippelen to be presented at ICONO'6, Tucson, Dec. (2001).
- 2) "Photorefractive polymers sensitized by two-photon absorption," B. Kippelen, P. A. Blanche, C. Fuentes-Hernandez, J. A. Herlocker, A. Schulzgen, B. Domercq, Y. F. Wang, S. R. Marder, N. Peyghambarian, Organic Thin Films for Photonic Applications, OSA annual meeting, Long Beach, October (2001).
- 3) "Nonlinear organic photorefractive polymers and their applications," B. Kippelen, International Workshop on Photonic Materials for the New Century, San Sebastian, Spain, May 27-31, Spain (2001).
- 4) "Photorefractive polymers for all optical storage and processing" B. Kippelen, presented at the ACFAS meeting held in Quebec, May 14-15, (2001).
- 5) *"Nonlinear organic photorefractive polymers and their applications,"* B. Kippelen, presented at the 200th Meeting of the Electrochemical Society held in San Francisco, Sept. 2-7, (2001).
- 6) "Nonlinear organic photorefractive polymers and their applications," B. Kippelen, International Conference on Dynamical Processes in Excited States of Solids, held in Lyon, France, July 1-4, (2001).
- 7) "Novel electro-active and light-emitting organic materials," B. Kippelen, B. Domercq, J. A. Haddock, C. Fuentes, P. A. Blanche, J. F. Wang, N. Peyghambarian, C. Grasso, M Halik, R. Hreha, S. R. Marder, presented at the E-MRS Spring meeting, Strasbourg, June (2001).
- 8) "Polymer dispersed liquid crystals for optical processing and lighting applications," B. Kippelen, A. Golemme, J. N. Haddock, C. Fuentes-Hernandez, presented at the SPIE annual meeting, San Diego (2001).
- 9) "Nonlinear organic photorefractive polymers and their applications," B. Kippelen, NOMA 2001, May 20-27, Cetraro, Italy (2001).
- 10) "Materials for Plastic Electronics," B. Kippelen, Workshop on Plastic Electronics, Corning, October 15, (2001).
- 11) "Polymer Optics," Arizona Research Forum, Nanotechnology, The University of Arizona, March 21, (2001).
- 12) "Polymer Optics," University of Washington, Seminar Series in Materials Science, Seattle, Feb. 26 (2001).

- 13) "Polymer Optics: Photorefractivity, Light-emission, and Lasing," B. Kippelen, Nonlinear Optics, Materials, Fundamentals, and Applications, Hawaii, August 7-10, (2000).
- 14) "Optical polymers with electro-active and electroluminescent properties," Annual meeting of the French Chemical Society, Rennes, September, France (2000).
- 15) "100% photogeneration efficiency in charge transfer complexes formed between low ionization potential arylamines and C₆₀," B. Kippelen, E. Hendrickx, S. Thayumanavan, S. R. Marder, A. P. Persoons, and N. Peyghambarian, Organic Photorefractive Materials VI, SPIE, San Diego, July 30, (2000).
- 16) "Electro-active and light-emitting polymers," Fall Review of the NSF Center COEDIP, University of Maryland, College Park, Nov. 30, (2000).
- 17) "Plastics for the Information Age," Arizona Research Forum, Optical Engineering Research, The University of Arizona, Nov. 16, (2000).
- 18) "Recent advances in electro-active and light-emitting polymers," 3M Corporation, Minneapolis/St. Paul, November 14, (2000).
- 19) "Recent advances in photorefractive and electroluminescent polymers," University of Munich, June (2000).
- 20) "Photorefractive and light-emitting polymers: from materials to applications," B. Kippelen, G. E. Jabbour, D. Pardo, S. E. Shaheen, J. F. Wang, Y. Zhang, E. Hendrickx, K. B. Ferrio, J. A. Herlocker, N. Peyghambarian, S. Thayumanavan, S. R. Marder, D. L. Mathine, H. S. Woo, N. R. Armstrong, to be presented at the third ICRS International Symposium, Future Aspects of Photonics Technologies, Sendai, November 24-26, Japan (1999).
- 21) "High speed photorefractive polymers," N. Peyghambarian, K. B. Ferrio, J. A. Herlocker, E. Hendrickx, B. D. Guenther, B. Kippelen, International Conference on Science and Technologies of Advanced Polymers, Yamagata, July 26-30, Japan, (1999).
- 22) "Improving the speed of organic photorefractive polymer composites," B. Kippelen, E. Hendrickx, K. B. Ferrio, J. Herlocker, Y. Zhang, S. R. Marder, S. J. Anderson, N. R. Armstrong, and N. Peyghambarian, SPIE, Denver, (1999).
- 23) "Photorefractive polymers with high speed," N. Peyghambarian, K. B. Ferrio, J. Herlocker, E. Hendrickx, B. D. Guenther, S. Mery, Y. Zhang, B. Kippelen, Mat. Res. Symp. Proc. Vol. 561 p. 131-139, (1999).

- 24) "Recent advances in photorefractive and electroluminescent polymers," Northwestern University, Chicago, September 27, (1999).
- 25) "Towards an organic optoelectronics technology: recent advances in photorefractive and electroluminescent polymers," B. Kippelen, VUB, University of Bruxelles, Belgium, June 29, (1999).
- 26) "Towards an organic optoelectronics technology: recent advances in photorefractive and electroluminescent polymers," B. Kippelen, Thomson-CSF, LCR, Chateau de Corbeville, June 25, (1999).
- 27) "Towards an organic optoelectronics technology: recent advances in photorefractive and electroluminescent polymers," B. Kippelen, Corning Europe, Avon, France, June 24, (1999).
- 28) "Towards an organic optoelectronics technology: recent advances in photorefractive and electroluminescent polymers," B. Kippelen, IPCMS, University of Strasbourg, France, June 17, (1999).
- 29) "Organic Photonic Materials and Technologies," B. Kippelen, Militarily Critical Technologies Review, Institute for Defense Analysis Review, Tucson, May 18, (1999).
- 30) "Polymer optoelectronics," B. Kippelen, Materials Chemistry Initiative, Southern University at Carbondale, 2nd Annual Southern Illinois Materials Chemistry Conference, October 24, (1999).
- 31) "Recent advances in organic light-emitting diodes," The Knowledge Foundation, San Diego, April 26, (1999).
- 32) "Polymer photonics," B. Kippelen, Arizona/Los Alamos Days meeting, Applied Mathematics Department, The University of Arizona, Tucson, January (1999).

CATEGORICAL EXCLUSION

The YORK UNIVERSITY and D. REGAN
(Name of Proposing Institution) (Name of Investigator)
hereby certify as follows:

1. All research to be performed under the proposal for research on VISUAL SENSITIVITIES
will be confined to the laboratory, except as disclosed below: AND DISCRIMINATIONS
(Research Title)

2. The research will not involve the use, manufacture, testing, or disposal of toxic, hazardous, or radioactive materials, except as disclosed below:

3. If the proposed research does involve any such materials, they will be disposed of in accordance with all applicable statutes and regulations.

4. The proposed research is not expected to have a significant impact on the quality of the human environment, except as otherwise disclosed below:

5. The proposed research does not involve construction of research or test facilities.

6. The proposed research is expected to conform to the provisions of the Clean Air Act and any implementation plans thereunder, as well as the Federal Water Pollution Control Act, and any permits issued or required thereunder. No facilities to be used in the research are on the EPA list of violating facilities.

7. The proposed research will not involve or affect endangered species, designated pursuant to the Endangered Species Act, or historical sites which are protected under National Historic Preservation Act procedures, except as disclosed below:

The parties signing this certification below understand that the Air Force Office of Scientific Research will rely on the certification in making determinations under the Air Force Environmental Impact Analysis Process and whether the proposed research qualifies for a categorical exclusion.

Suzanne Macdonald
(Signature of Authorized Official of Institution)

D. Regan
(Signature of Principal Investigator)

Mac/b02
(Date)

28 Feb. 2002
(Date)

The National Environmental Policy Act of 1969 (NEPA) requires Federal agencies to consider potential environmental concerns of major federal undertakings. This includes research projects funded by the Air Force Office of Scientific Research (AFOSR). Under the Air Force Environmental Impact Analysis Process, all projects must have an environmental assessment or environmental impact statement completed UNLESS they qualify for a categorical exclusion from this requirement. In order to qualify for this categorical exclusion, proposed research must be normal and routine basic or applied research confined to the laboratory and in compliance with all safety, environmental, and natural resource conservation laws. The following documentation must be completed in order to assist AFOSR in determining whether the proposed research meets the criteria for such categorical exclusion.

The York University and D. Regan
(Name of Proposing Institution) (Name of Investigator)
hereby certify as follows:

1. All research to be performed under the proposal for research VISUAL SENSITIVITIES AND DISCRIMINATIONS
(Research Title)

will be confined to the laboratory, except as disclosed below:

2. All research identified in number 1 above, will be conducted in compliance with all safety, environmental, and natural resource conservation laws, except as disclosed below

3. The proposed research does not involve major construction or remodeling of buildings used as research or test facilities.

4. Any additional information that will assist AFOSR in accomplishing the required environmental determination:

The parties signing this certification below understand that the Air Force Office of Scientific Research will rely on the certification in making determinations under the Air Force Environmental Impact Analysis Process and whether the proposed research qualifies for a categorical exclusion.

Suzanne Macdonald
(Signature of Authorized Official of the Institution)

D. Regan
(Signature of Principal Investigator)

March 6/02
(Date)

11 Feb. 2002
(Date)